

The performance of a soluble lead-acid flow battery and its comparison to a static lead-acid battery

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ABSTRACT

The electrochemistry of static lead-acid and soluble lead-acid flow batteries is summarised and the differences between the two batteries are highlighted. A general comparison of the performance of an unoptimised soluble lead-acid flow laboratory cell and a commercial lead-acid battery during charge and discharge is reported. The influence of the depth of discharge on cycle life for both batteries is also considered. The flow battery was found to have a better charge efficiency than the static one, but the cells were found to have comparable energy efficiencies. The self-discharge characteristics of the soluble lead-acid battery were also measured and compared to reported values for a commercial static battery. Some self-discharge of the soluble lead-acid flow battery is observed during prolonged periods on open-circuit but the battery could recover its normal performance after a single charge–discharge cycle.

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1. Introduction

Large scale energy storage has been the subject of significant research and development in recent years, stimulated by the need to integrate large-scale renewable resources. Energy storage is also needed for load levelling, peak shaving and uninterruptable power supply (UPS) applications. Alternative energy storage systems have been considered, including batteries, fuel cells and flywheel energy storage systems [1–6]. Low cost, long life and reliability are key attributes of suitable energy storage systems.

Static lead-acid batteries, which were developed in 1859 by Planté, were first demonstrated at the French Academy of Sciences in 1860 [7]. After nearly 150 years since their invention, such batteries still play a vital role and are routinely used in automotive applications and as the direct current power supply for electric vehicles due to their versatility, high reliability, high discharge rate, flexible performance and ease of recycling. However, static lead-acid batteries are not well suited for large-scale energy storage because of their high cost, restricted shelf-life, and practical difficulties in building large batteries.

Flow batteries, which are relatively new energy storage devices, provide an alternative solution to the problem of balancing power generation and power consumption (e.g. load levelling and peak

shaving) [8,9]. They could also be key enabling elements for the exploitation of clean renewable energy sources [9,10] as they are needed to cope with the unavailability or unpredictability of solar and wind resources.

A number of redox couples have been proposed for use within large-scale flow batteries. Operational flow battery technologies include bromine/polysulfide [11], all vanadium [12,13], vanadium–bromine, [14] zinc/bromine [15] and zinc/cerium [16], which are in various stages of development. However, it is believed that if any of these technologies are commercially successful, the implications for the electricity industry could be significant.

In 2004, Pletcher et al. proposed the soluble lead-acid flow battery, and a subsequent series of research papers have been published concerning the chemistry, electrochemistry, engineering and performance of this battery [17–28]. The battery is based on the electrode reactions of Pb(II) in methanesulfonic acid; the electrode reactions of the cell are shown in Table 1. The principle of operation and cell construction of the soluble lead-acid flow battery system are shown in Fig. 1. The system consists of an electrolyte tank filled with lead(II) ions in a methanesulfonic acid solution. The electrolyte is continuously pumped through a cell stack. During charge, lead is deposited on the negative electrode while lead dioxide is deposited on the positive one. During discharge, the lead and lead dioxide layers re-dissolve via oxidation and reduction, respectively, back to the soluble Pb(II) ion. Electrochemical measurements have shown that both the Pb/Pb²⁺ and Pb²⁺/PbO₂ redox couples are suitable for use with a methanesulfonic acid electrolyte and substantial lead and lead

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Nomenclature

<i>Symbol</i>		$\Delta_r S$	entropy change for the cell reaction (J K^{-1})
E_{cell}^e	equilibrium cell voltage (V)	T	temperature (K)
E_{cell}	cell voltage (V)	z	number of electrons involved in the cell reaction
$E_{\text{cell}}^{\text{o.c.}}$	open-circuit cell voltage (V)	η_c	charge efficiency of battery
F	Faraday constant, $96,485 \text{ (C mol}^{-1}\text{)}$	η_e	energy efficiency of battery
$\Delta_r G$	Gibbs free energy change for the cell reaction (J mol^{-1})	$(\eta_{\text{mt}})_+$	mass transport polarisation at the positive electrode (V)
$\Delta_r H$	standard enthalpy change for the cell reaction (J mol^{-1})	$(\eta_{\text{mt}})_-$	mass transport polarisation at the negative electrode (V)
I	cell current (A)	$(\eta_{\text{ct}})_+$	charge transfer polarisation at the positive electrode (V)
R_i	internal resistance of cell (Ω)	$(\eta_{\text{ct}})_-$	charge transfer polarisation at the negative electrode (V)
R	molar gas constant, $8.314 \text{ (J K}^{-1} \text{ mol}^{-1}\text{)}$		

Table 1

Electrode processes of static lead-acid and soluble lead-acid flow batteries.

Feature	Static lead-acid battery	Soluble lead-acid flow battery
Material of negative electrode	Lead (pure lead metal)	Lead (electrodeposited on an inert substrate, e.g. nickel)
Material of positive electrode	Lead dioxide (lead oxidised by Barton pot or ball mill)	Lead dioxide (electrodeposited on an inert substrate, e.g. carbon polymer)
Electrolyte	High concentration of sulphuric acid	Aqueous methanesulfonic acid
Negative electrode reaction	$\text{Pb} \xrightleftharpoons[\text{Charge}]{\text{Discharge}} \text{Pb}^{2+} + 2\text{e}^-$ $\text{Pb}^{2+} + \text{SO}_4^{2-} \xrightleftharpoons[\text{Charge}]{\text{Discharge}} \text{PbSO}_4$	$\text{Pb} \xrightleftharpoons[\text{Charge}]{\text{Discharge}} \text{Pb}^{2+} + 2\text{e}^-$
Standard potential of the negative electrode reaction (V)	−0.36 [19]	−0.13 [3]
Positive electrode reaction	$\text{PbO}_2 + 4\text{H}^+ + 2\text{e}^- \xrightleftharpoons[\text{Charge}]{\text{Discharge}} \text{Pb}^{2+} + 2\text{H}_2\text{O}$ $\text{Pb}^{2+} + \text{SO}_4^{2-} \xrightleftharpoons[\text{Charge}]{\text{Discharge}} \text{PbSO}_4$	$\text{PbO}_2 + 4\text{H}^+ + 2\text{e}^- \xrightleftharpoons[\text{Charge}]{\text{Discharge}} \text{Pb}^{2+} + 2\text{H}_2\text{O}$
Standard potential of the positive electrode reaction (V)	1.69 [19]	1.49 [3]
Cell reaction	$\text{PbO}_2 + \text{Pb} + 2\text{H}_2\text{SO}_4 \xrightleftharpoons[\text{Charge}]{\text{Discharge}} 2\text{PbSO}_4 + 2\text{H}_2\text{O}$	$\text{PbO}_2 + \text{Pb} + 4\text{H}^+ \xrightleftharpoons[\text{Charge}]{\text{Discharge}} 2\text{Pb}^{2+} + 2\text{H}_2\text{O}$
Gibbs free energy change for cell reaction (kJ mol^{-1})	−394	−313
Standard cell voltage (V)	2.04 [19]	1.62 [3]
Typical operating temperature range (K)	−253 to 313 [20]	273–313 [10]
Intended applications	Small scale automotive, standby power suppliers	Potential energy storage, e.g. load-levelling, peak shaving and uninterruptable power supplies

dioxide layers could be reversibly deposited and stripped from a number of electrode materials.

It can be seen clearly that the chemistry of this battery differs from the traditional lead-acid battery as Pb(II) is highly soluble in the methanesulfonic acid electrolyte and the electrode reactions do not involve insoluble Pb(II). It also differs from all existing flow battery technologies since it employs only a single electrolyte and therefore operates without a membrane separator; this reduces its cost and design complexity significantly. The absence of a membrane also has a positive influence on the energy efficiency and the cell chemistry avoids the problems associated with leakage and cross-contamination of species through a membrane that have severely hampered other flow battery technologies.

All the experiments with the small flow cell in laboratory confirm that this flow battery is a promising concept, typically with a coulombic efficiency >85%, an energy efficiency of around 65% and an open circuit voltage of 1.69 V.

To assess the performance of the soluble lead-acid flow battery, this paper attempts a direct comparison, based on experimental tests, between a non-optimised laboratory soluble lead-acid flow battery and a commercial static lead-acid battery. Analysis of charge and discharge characteristics over many cycles is used to determine energy, charge and voltage efficiencies of both batteries. Cycle life and self-discharge for both batteries are also analysed. Fi-

nally, the environmental impact of soluble lead-acid flow batteries is considered.

2. Electrode processes

Table 1 shows the comparative electrochemical characteristics of the static and soluble lead-acid batteries. The static lead-acid battery uses lead dioxide as an active material on the positive electrode (usually as a porous, pasted material), metallic lead, in a high-surface-area porous structure, as the negative electrode active material and sulphuric acid, typically 4 mol dm^{-3} as the electrolyte. Static lead-acid batteries involve sulphate formation on each electrode during discharge. Due to water formation on discharge, the specific gravity reduces and lead sulphate is gradually deposited on the electrodes. During charge the processes are reversed. The lead sulphate transforms to PbO_2 on the positive electrode and Pb on the negative electrode, respectively. PbO_2 and Pb are deposited on both electrodes gradually and the specific gravity increases.

The solution of the soluble lead-acid flow cell consists of lead (II) methanesulfonate (PbMSA), methanesulfonic acid (MSA), hexadecyltrimethylammonium hydroxide (HDTMAH) used as an aqueous surfactant dispersion. The cell used carbon-polymer com-

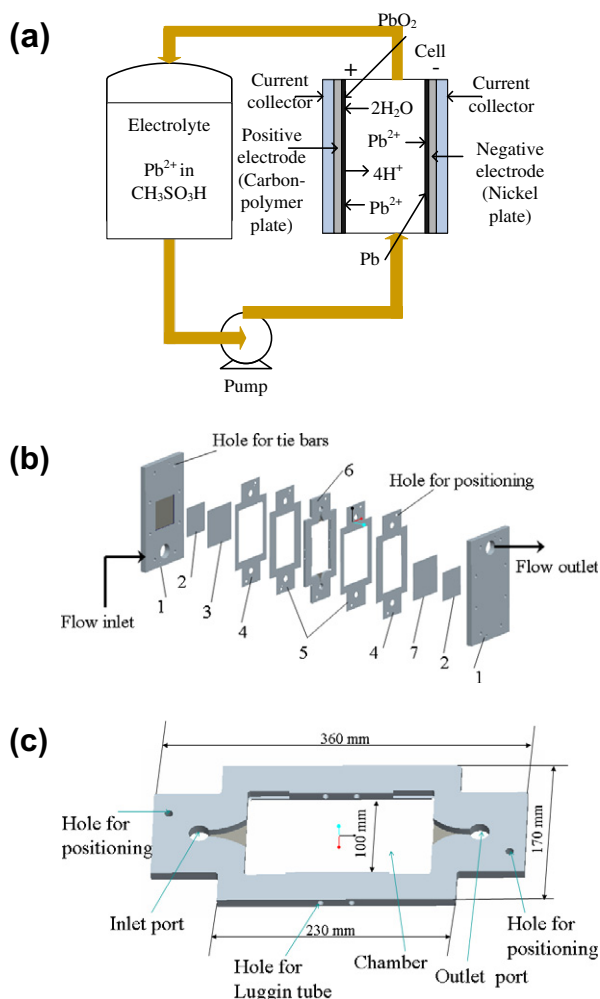


Fig. 1. (a) The principle of a soluble lead-acid flow battery (the cell is shown on charge). (b) Cell construction of the soluble lead-acid battery (exploded view) (1) stainless steel end plate (36.5 cm × 21 cm × 2 cm); (2) current collector (copper, 10 cm × 10 cm); (3) negative electrode (nickel, 13 cm × 13 cm); (4) electrode containing frames (polypropylene); (5) frame gaskets; (6) electrolyte chamber frame (polypropylene); (7) positive electrode (carbon-polymer composite, 13 cm × 13 cm). (c) The electrolyte chamber frame.

posite as the positive electrode and metal nickel as the negative electrode. During charging, lead(II) is reduced to lead on the negative electrode and oxidised to lead dioxide on the positive electrode. On discharge, lead and lead dioxide dissolve, forming lead(II), which re-dissolves in the electrolyte. The kinetics of electrode reactions associated with reduction and oxidation of soluble lead-acid flow cell species are complex. They can involve electron transfer, diffusion, chemical reactions, phase transformation between solid state and liquid state, and adsorbed intermediates. Since the system is sufficiently stirred by electrolyte circulation during cell operation, the mass transport is not a factor in determining the current. Instead current is mainly controlled by charge transfer, in which the current density is related exponentially to the overpotential.

From Table 1, the potential of the PbSO_4/Pb couple in sulphuric acid is lower than that of Pb^{2+}/Pb couple in the methanesulfonic acid at a concentration of 1 mol dm^{-3} . The potential of $\text{PbSO}_4/\text{PbO}_2$ is above that of the $\text{Pb}^{2+}/\text{PbO}_2$ couple.

For the static lead-acid battery, the solid PbSO_4 phase is more stable than dissolved Pb^{2+} in the electrolyte. The standard free energy change for the conversion of PbSO_4 to Pb and PbO_2 reactions is

bigger than that for the conversion of Pb^{2+} to Pb and PbO_2 ; this indicates that it is thermodynamically less favourable for the conversion of PbSO_4 to Pb and PbO_2 . Therefore, during charge, the static lead-acid battery reaction needs a larger cell voltage to transform the PbSO_4 phases to Pb and PbO_2 than the soluble lead-acid flow battery.

3. Experimental details

The battery testing system is shown schematically in Fig. 2. A TTI programmable charger and an electronic load were used to carry out the charge and discharge tests. The charger and electronic load are capable of charging and discharging the battery at a maximum rate of 10 A and 80 A, respectively. They can operate in several modes: constant current mode, constant voltage mode, constant resistance mode and constant power mode. A National Instrument (NI) USB-6225 was used to measure the battery voltage. A Labview software interface was used to set the current on the programmable charger and load, set the charging time and set the discharge time or voltage limits.

The cell construction of the soluble lead-acid flow battery is shown in Fig. 1b. The positive and negative electrodes were carbon polyvinyl-ester composite (Entegris) and nickel plate (Goodman Alloys Ltd.), respectively. Both electrodes were $13 \text{ cm} \times 13 \text{ cm}$ plates and secured to current collectors (copper plates, $10 \text{ cm} \times 10 \text{ cm}$) using a polypropylene frame (TM Plastics Ltd.) and then masked using an adhesive insulating tape to protect the copper from corrosion, giving an exposed electrode areas $10 \text{ cm} \times 10 \text{ cm}$. The inter-electrode gap of 1.2 cm was established using polypropylene frame and elastomeric EPDM gaskets (Klinger) which are inserted between the frames to seal the cell. Fig. 1c shows a 3D view of the electrolyte chamber frame ($36 \text{ cm} \times 17 \text{ cm} \times 1 \text{ cm}$). The electrolyte frame has holes drilled into the sides so that a Luggin tube could be inserted to monitor the individual electrode potentials [24]. The electrolyte comprised $1 \text{ mol dm}^{-3} \text{ Pb}(\text{CH}_3\text{SO}_3)_2$, $0.5 \text{ mol dm}^{-3} \text{ CH}_3\text{SO}_3\text{H}$, and $0.005 \text{ mol dm}^{-3} \text{ C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}(\text{OH})$ and had a volume of 1.5 dm^3 , which was stored in a 2 dm^3 cylindrical reservoir and circulated through the system via a pump (Totton Pumps, type T113095) with a mean linear flow velocity of 2.3 cm s^{-1} past the electrode surfaces.

The static lead-acid battery used was a Lucas BAGM012-6 VRLA battery with 3 cells in series, suitable for general purpose use. The manufacturer's specifications were a nominal voltage of 6 V, a theoretical capacity 12 A h (20 h-rate) with a weight of 2.0 kg. The effective electrode area of the negative (and positive) plate was 364 cm^2 . The specifications of the two batteries are summarised in Table 2.

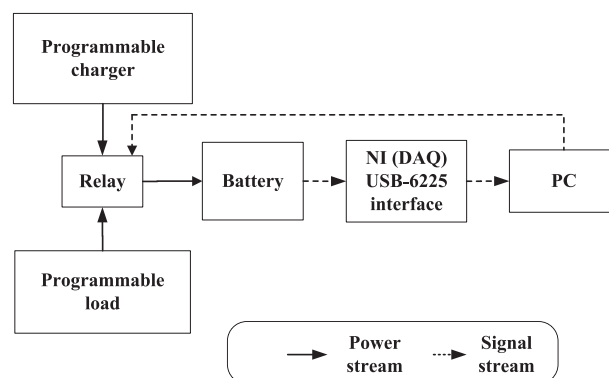


Fig. 2. The battery test system, showing the direct current power and signal connections.

Table 2

The specifications of a static lead-acid battery and a soluble lead-acid flow battery in this paper.

Type of battery	Number of electrodes	Nominal capacity (A h)	Nominal voltage (V)	Total area of each electrode (cm ²)
Static lead-acid battery	6	12	6	364
Soluble lead-acid flow battery	2	4	1.65	100

4. Results and discussion

4.1. Charge characteristics

Fig. 3 shows the cell voltage vs. time behaviour during the first five charge/discharge cycles of the soluble lead-acid flow battery at a current density of 20 mA cm^{-2} . It is apparent from Fig. 3 that from the second cycle onwards, the charge voltage starts at a lower value and maintains a high constant value over a period of time. This feature was explained in a previous paper [18], and results from the remaining PbO_x on the positive electrode, which cannot be reduced further. PbO_2 deposits on top of this layer at potentials which are more negative than those for bulk deposition when the cell is charged again. It suggests that the residue favours the conversion of Pb^{2+} to PbO_2 . This effect is similar to the deposition of lead dioxide from a fluoboric acid electrolyte [29].

Fig. 4 shows the cell voltage vs. time charge characteristic of the two batteries at various currents. The soluble lead flow cell was charged at constant current in the range from 1 A to 6 A until the capacity was up to 4 A h. To avoid oxygen and hydrogen evolution, the commercial lead-acid battery was first charged at constant current until the battery voltage reached maximum charge voltage, then was charged at the maximum voltage till the charge current dropped to 0.3 A. From the data in Fig. 4 we can find that the overpotential for both batteries associated with ohmic loss and polarisation at the electrodes increases with current density as expected. However, the charge curves for the two batteries are rather different. For the soluble lead-acid flow cell, considering the 2 A charge curve, the cell voltage vs. time response during charge is

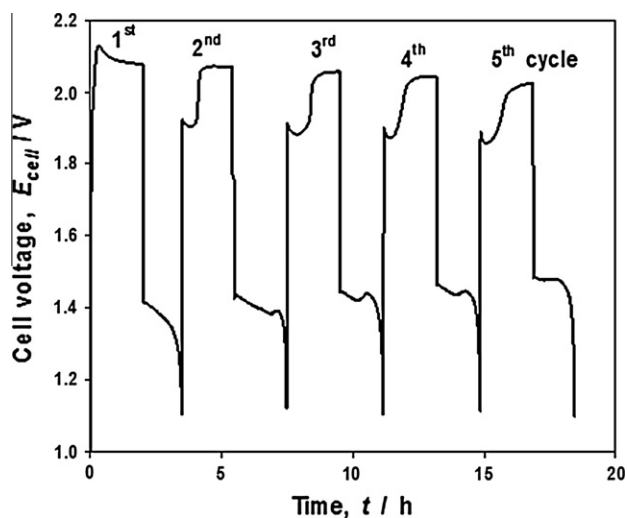


Fig. 3. Cell voltage vs. time for the first five charge/discharge cycles of the soluble lead-acid flow battery. In each cycle, the current density on charge and discharge was 20 mA cm^{-2} . Electrolyte: $1 \text{ mol dm}^{-3} \text{ Pb}(\text{CH}_3\text{SO}_3)_2 + 0.5 \text{ mol dm}^{-3} \text{ CH}_3\text{SO}_3\text{H} + 0.005 \text{ mol dm}^{-3} \text{ C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}^+$; electrolyte linear flow velocity: 2.3 cm s^{-1} ; temperature: 298 K.

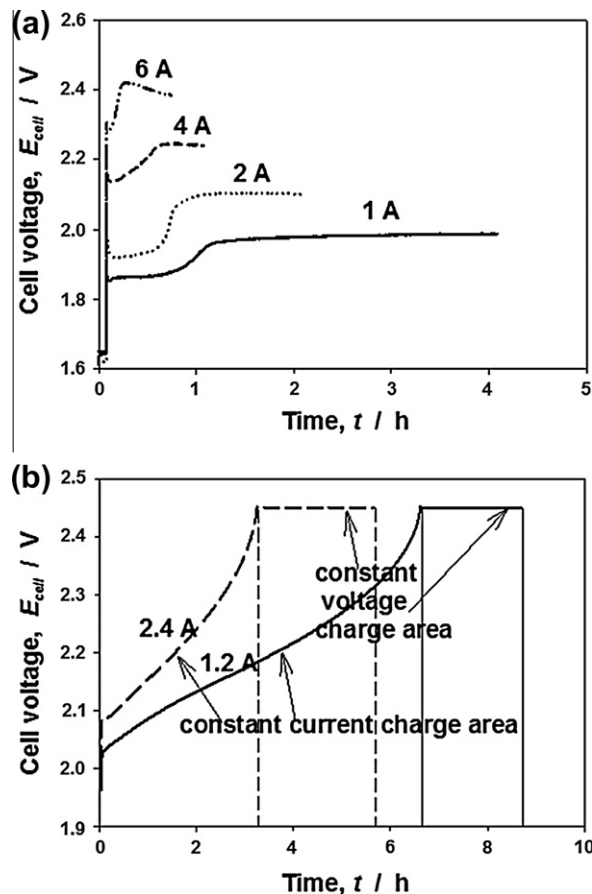


Fig. 4. (a) Soluble lead-acid flow battery. Cell voltage vs. time curves as a function of charge current. In each case, the cell was discharged at 2 A until the voltage dropped to 0.8 V. The electrolyte contained $1 \text{ mol dm}^{-3} \text{ Pb}(\text{CH}_3\text{SO}_3)_2$ and $0.5 \text{ mol dm}^{-3} \text{ CH}_3\text{SO}_3\text{H}$ plus $0.005 \text{ mol dm}^{-3} \text{ C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}^+$. Electrolyte linear flow velocity was 2.3 cm s^{-1} . (b) Static lead-acid battery. Cell voltage vs. time curves as a function of charge current. In each case, the cell was discharged at 2 A until the battery voltage dropped to 5.25 V (equivalent to 1.75 V per cell); temperature: 298 K.

complex as discussed earlier [18]. For the static lead-acid battery, the charge voltage keeps increasing all the time during constant current charge stage. This is a result of the gradual increase of the concentration of sulphuric acid during charging.

4.2. Discharge characteristics

In the experiments, when connected to an external load, the cell voltage E_{cell} can be expressed as:

$$E_{\text{cell}} = E_{\text{cell}}^{\text{o.c.}} - [(\eta_{\text{mt}})_+ + (\eta_{\text{ct}})_+] + [(\eta_{\text{mt}})_- + (\eta_{\text{ct}})_-] - IR_i \quad (1)$$

where $E_{\text{cell}}^{\text{o.c.}}$ is the open-circuit cell voltage; $(\eta_{\text{mt}})_+$, $(\eta_{\text{mt}})_-$ denote mass transport or concentration polarisation overpotentials at the positive and negative electrodes, respectively; $(\eta_{\text{ct}})_+$, $(\eta_{\text{ct}})_-$ are charge transfer or activation polarisation overpotentials at positive and negative electrodes, respectively; I is the operating current of cell, R_i is the internal resistance of the cell.

As shown in Eq. (1), the effective voltage delivered by the cell is reduced by polarisation and Ohmic losses. It should be noted that the overpotential caused by activation and concentration polarisations increases with current density, just as the IR drop. The total internal impedance of a cell is the sum of the resistances across the solution and in the external circuit.

Fig. 5a and b shows a comparison of discharge characteristics at various current densities for both batteries at room temperature. In each case, the soluble lead-acid flow battery was charged for 2 h at the current density of 20 mA cm^{-2} . The static lead-acid battery was charged at 1.2 A until the cell voltage increased to 2.45 V, then charged at a constant voltage of 2.45 V per cell until the current dropped to 0.3 A. From the data in Fig. 5, it is evident that at low current densities, the soluble lead-acid flow battery maintains a flatter cell voltage vs. time behaviour during most of the discharge process than the static lead-acid battery; the cell voltage remains almost constant until one of the active materials is fully consumed. As expected, the overpotentials in both batteries increase with current density, however, they are higher for the unoptimised soluble lead-acid flow battery compared to the static lead-acid battery at the same current density. The overpotentials, per cell at the start of discharge for the static lead-acid battery, from a fully charged state, were 0.14 V and 0.21 V at 20 mA cm^{-2} and 40 mA cm^{-2} , respectively. The overpotentials for the soluble lead-acid flow battery were estimated to be 0.3 V and 0.44 V, respectively, which are largely due to ohmic loss, which is significantly higher than that of the static battery. This loss may be reduced by optimising cell design and operation conditions.

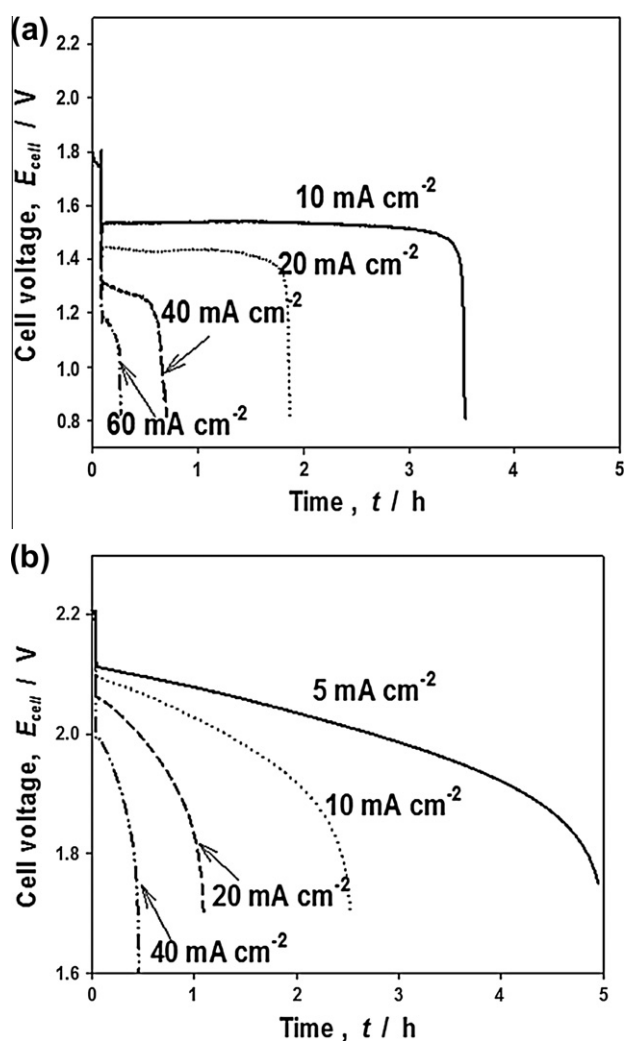


Fig. 5. (a) Soluble lead-acid flow battery. Cell voltage vs. time curves as a function of discharge current densities. The electrolyte contained $1 \text{ mol dm}^{-3} \text{ Pb}(\text{CH}_3\text{SO}_3)_2$ and $0.5 \text{ mol dm}^{-3} \text{ CH}_3\text{SO}_3\text{H}$ plus $0.005 \text{ mol dm}^{-3} \text{ C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}^+$. Electrolyte linear flow velocity: 2.3 cm s^{-1} . (b) Static lead-acid battery. Cell voltage vs. time curves as a function of discharge current densities; temperature: 298 K.

4.3. Cell efficiency

The main engineering figures of merit defined for both static lead-acid batteries and soluble lead-acid flow batteries are charge efficiency and energy efficiency.

The charge efficiency is the ratio of electrical charge provided by the battery during discharge compared to that supplied during charge,

$$\eta_c = \frac{Q_{\text{Discharge}}}{Q_{\text{Charge}}} \quad (2)$$

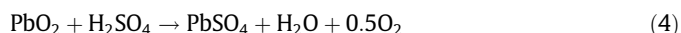
The energy efficiency is the ratio of energy between the discharge and charge processes,

$$\eta_e = \frac{E_{\text{Discharge}}}{E_{\text{Charge}}} \quad (3)$$

Table 3 reports the average voltage, charge and energy efficiencies for the two batteries at various discharge current densities. It can be seen that both batteries have similar energy efficiencies for current densities of 10, 20 and 40 mA cm^{-2} , but the soluble lead-acid has a higher charge efficiency. The charge efficiency and energy efficiency of the soluble lead-acid flow battery are severely reduced at the current density of 60 mA cm^{-2} . This does not mean that all the active material has been consumed and it is possible to continue to discharge the battery at a lower current density [30].

4.4. Self-discharge characteristics

For static lead-acid batteries, the lead and lead dioxide are thermodynamically unstable in sulphuric acid solutions. The potential of $\text{PbO}_2/\text{PbSO}_4$ couple is 1.69 V above that of $\text{O}_2/\text{H}_2\text{O}$ couple (1.229 V), and the potential of Pb/PbSO_4 couple is 0.356 V below that of the $\text{H}_2/\text{H}_2\text{O}$ couple [31]. On the shelf, with the passage of time, lead sulphate forms at both electrodes according to reactions (6) and (7).



The rates of these gassing reactions depend on the O_2 overvoltage on the positive electrode and the H_2 overpotential on the negative electrode, respectively. As a result, the active materials are consumed and the available charge capacity is gradually lost during storage. The rate of self-discharge can be rapid at high states of charge; the normal self-discharge for VRLA batteries is typically 15% of nominal capacity per month at 25°C [32], but it is faster at higher temperatures.

Self-discharge was also observed in the case of the soluble lead-acid flow battery when it was left open-circuit for a long time per-

Table 3

Performance of the static lead-acid battery and the soluble lead-acid flow battery as a function of discharge current density, temperature: 298 K.

Current density (mA cm^{-2})	Average discharge cell voltage (V)		% Charge efficiency		% Energy efficiency	
	Static lead-acid battery	Soluble lead-acid flow battery	Static lead-acid battery	Soluble lead-acid flow battery	Static lead-acid battery	Soluble lead-acid flow battery
5	2	–	96	–	86	–
10	1.99	1.52	87	88	78	69
20	1.96	1.42	74	95	65	68
40	1.91	1.23	59	71	51	46
60	–	1.13	–	37	–	21

iod. To test the self-discharge characteristic of a soluble lead-acid flow battery, a series of charge/discharge cycles were performed. For each cycle, the cell was charged at 20 mA cm^{-2} for 2 h, followed by discharge to 1.10 V at the same current density. After several charge/discharge cycles, the cell was charged at 20 mA cm^{-2} for 2 h, then left on open-circuit, while the pump was switched off and the electrolyte remained still in the cell. After 44 h, the pump was switched on again and the cell was discharged at the same current density till the cell voltage dropped to 1.10 V. This was followed by a series of charge/discharge cycles. The cell voltage as a function of time for the two discharge conditions is shown in Fig. 6: curve (a) shows the discharge voltage characteristics immediately after the end of charging, and curve (b) shows the discharge voltage characteristics after being left open-circuit for 44 h. The charge efficiencies for two discharges were 93% and 71%, respectively. Self discharge is thought to result from oxidation of Pb by O_2 and reduction of PbO_2 by the acid, forming insoluble Pb^{2+} species. However, it was found that the cell can recover to normal performance following one charge and discharge cycle.

In addition to the above test, the open-circuit cell voltage was observed at the end of the charging period, while the cell was at a temperature of 298 K as shown in Fig. 7. The open-circuit voltage for the soluble lead-acid flow battery is determined by the Nernst equation:

$$E_{\text{cell}} = E_{\text{cell}}^0 + \frac{RT}{2F} \ln \frac{[\text{H}^+]^4}{[\text{Pb}^{2+}]^2} \quad (6)$$

The open-circuit cell voltage is a function of electrolyte concentration and temperature according to Eq. (6). From Fig. 7, we can see that the cell voltage decreases remarkably for the first 2 h, decreasing at a rate of 59 mV per hour, which indicates that the proton and Pb^{2+} concentrations continue to vary for a period of time before reaching equilibrium. A possible explanation for this phenomenon is that the proton and Pb^{2+} concentration on the electrodes during charge is quite different from those in the bulk solution [19], the equilibrium between the electrodes and the electrolyte requires diffusion over a long period of time. After the 2nd hour, the rate of decrease of the open-circuit cell voltage is much smaller at around 0.8 mV per hour, which suggests the cell was near a steady state. The decrease of the open-circuit cell voltage is thought to result mainly from self-discharge in the cell. Therefore the change of the

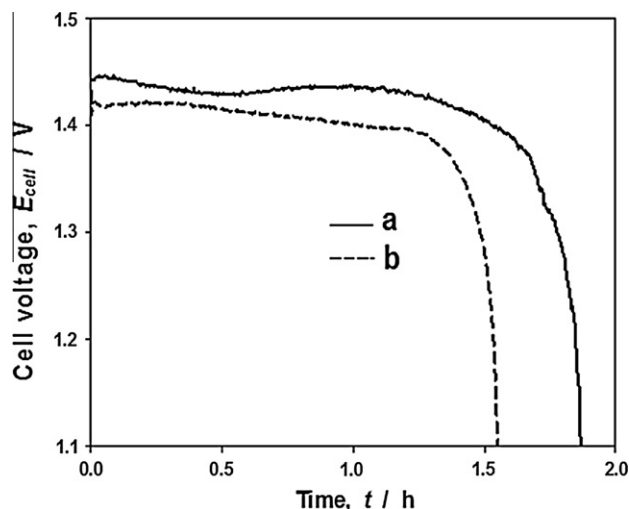


Fig. 6. Soluble lead-acid flow battery discharge voltage vs. time profile. (a): Discharge immediately after charge. (b): Discharge following 44 h at open-circuit. Electrolyte: $1 \text{ mol dm}^{-3} \text{ Pb}(\text{CH}_3\text{SO}_3)_2 + 0.5 \text{ mol dm}^{-3} \text{ CH}_3\text{SO}_3\text{H} + 0.005 \text{ mol dm}^{-3} \text{ C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}^+$; electrolyte linear flow velocity: 2.3 cm s^{-1} ; temperature: 298 K.

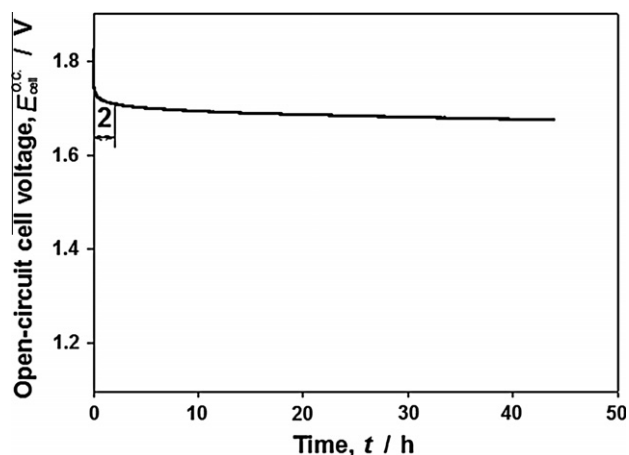


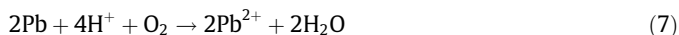
Fig. 7. Open-circuit cell voltage for a soluble lead-acid flow battery vs. time characteristic after the cell was charged for 2 h at 20 mA cm^{-2} ; temperature: 298 K.

open-circuit cell voltage during storage can be used as a guide to the degree of self-discharge.

4.5. Cycle life

Following a large number of charge/discharge cycles, a soluble lead-acid flow battery could fail due to cell shorting caused by the growth of lead and lead dioxide deposition the negative and positive electrode, respectively. Fig. 8 shows the cycle characteristics of soluble lead-acid in diagrammatic form. Fig. 9 reports its relative efficiencies as a function of cycle number. From the data in Fig. 8a, we can find that the cell begins to exhibit shorting between the electrodes at the 46th cycle. The shorting behaviour of the cell is illustrated in Fig. 8b. The charge efficiency is approximately 80% for the first 45 cycles. From the 46th cycle; the charge efficiency drops sharply, as shown in Fig. 9. The voltage efficiency increases gradually, from the first few cycles, to a steady value during the last 30 cycles. During cycling under constant current conditions, the cell performance was steady.

To remove shorting and maintain the battery performance, one approach is to dissolve lead and lead dioxide back to solutions after a number of charge/discharge cycles using non-electrochemical reactions without any additional irreversible chemicals. Oxygen has been proposed. This chemical is used for balancing the cell since the reaction on the negative electrode has higher charge efficiency and more lead remains on the negative electrode than lead dioxide on the positive electrode after several charge/discharge cycling [19]. The reaction is expressed as



The lead remaining on the electrode can be removed after adding oxygen. The cell can be reused after the oxygen treatment. A procedure involves the periodic addition of hydrogen peroxide to the electrolyte while the cell is in the discharged state has been reported to restore both the electrodes and electrolytes to their initial conditions and would be a promising approach to long term operation of the soluble lead acid flow battery [25].

Based on the manufacturer's data sheet, the life of the static lead-acid battery is around 1500 cycles when the battery is kept at room temperature and the depth of discharge (DOD) is limited to 30%. When the DOD is exceeded, the cycle life decreases dramatically. This is due to the occurrence of irreversible sulphation at the electrode plates during discharge, thus resulting in severe degradation of the battery's capacity. The influence of the depth of discharge on cycle life of the valve regulated lead-acid battery at

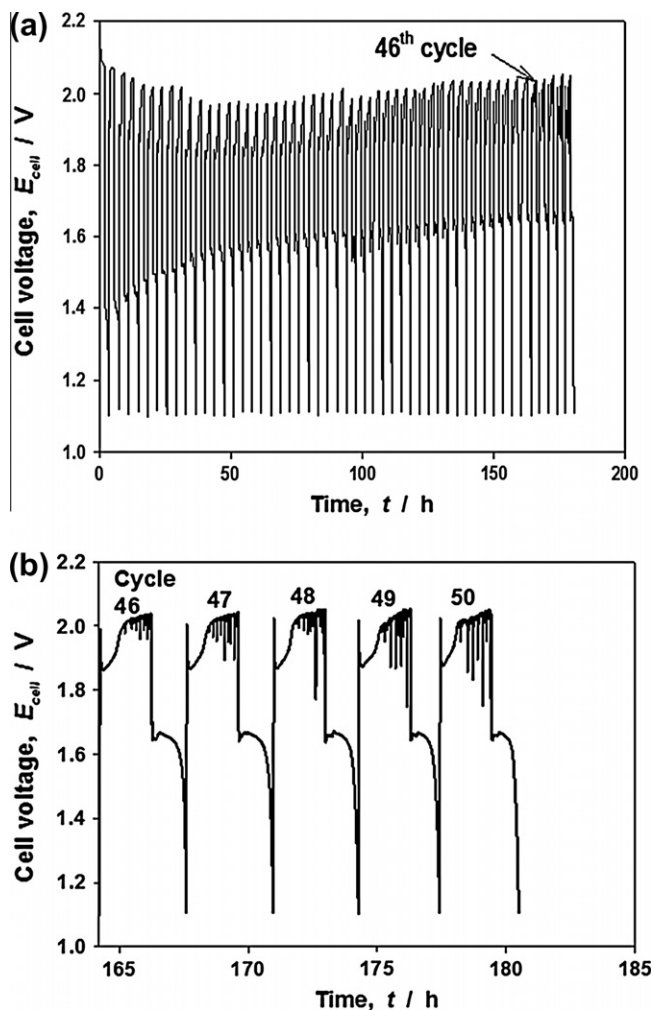


Fig. 8. (a) Cell voltage of a soluble lead-acid flow battery vs. time data for a number of charge/discharge cycles. In each cycle, the cell was charged for 2 h at 20 mA cm^{-2} then discharged at the same current density until the cell voltage dropped to 1.1 V. Electrolyte: $1 \text{ mol dm}^{-3} \text{ Pb}(\text{CH}_3\text{SO}_3)_2 + 0.5 \text{ mol dm}^{-3} \text{ CH}_3\text{SO}_3\text{H} + 0.005 \text{ mol dm}^{-3} \text{ C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}^+$; electrolyte linear flow velocity: 2.3 cm s^{-1} ; temperature: 298 K. (b) Self-shorting behaviour of the flow cell due to non-uniform deposit growth (enlargement of (a) from the 46th to 50th cycle).

constant conditions was described in details in [33]. The cycle service life of the battery at 100% DOD decreases 4 times compared to the cycle life at 30% DOD.

As described above, the cycle life of static lead-acid batteries is strongly influenced by the depth of discharge. To test whether the soluble lead-acid flow battery is affected by DOD, four experiments were conducted. In each experiment, the cell was charged at 20 mA cm^{-2} for 2 h with the charge capacity of 4 Ah considered as a nominal value. The cell was subsequently discharged at the same current density for a specified time (and specified charge) corresponding to a certain DOD (100%, 75%, 50% or 25%). However, the discharge was stopped earlier if the cell voltage fell below the cut-off value. The battery was subsequently recharged at the same current density for the same specified time. The charge and discharge cycles were repeated until the battery failed. In this paper, for soluble lead-acid flow battery, we consider the cell to have failed if the charge efficiency is below 80% when the current density is at 20 mA cm^{-2} . A summary of the experimental results is shown in Table 4. Fig. 10 illustrates the life cycle characteristic at different depth of discharge values, typically at 100% DOD, 16 cycles were reached. It demonstrates that a high cycle life can be achieved by reducing the depth of discharge.

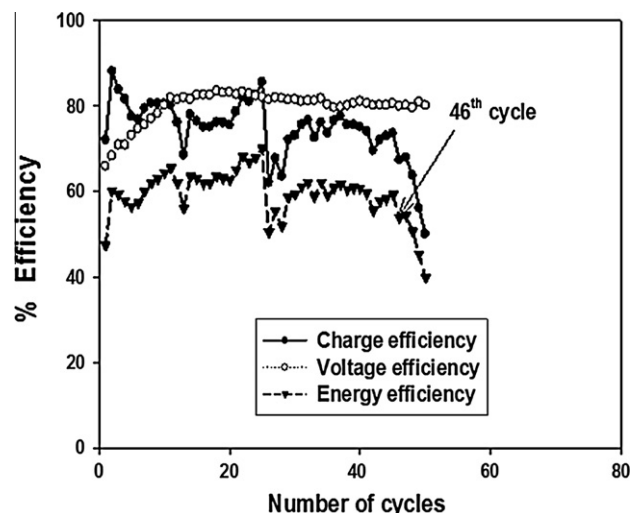


Fig. 9. Charge, voltage and energy efficiencies vs. number of cycles (<50) for a soluble lead-acid flow battery. Electrolyte: $1 \text{ mol dm}^{-3} \text{ Pb}(\text{CH}_3\text{SO}_3)_2 + 0.5 \text{ mol dm}^{-3} \text{ CH}_3\text{SO}_3\text{H} + 0.005 \text{ mol dm}^{-3} \text{ C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}^+$; electrolyte linear flow velocity: 2.3 cm s^{-1} ; temperature: 298 K.

Table 4

Summary of results for the soluble lead-acid flow battery at different DOD values, temperature: 298 K.

% Depth of discharge	Number of cycles	% Averaged charge efficiency over n cycles	% Averaged voltage efficiency over n cycles	% Averaged energy efficiency over n cycles
100	16	88	72	63
75	40	88	73	64
50	65	91	74	67
25	80	97	70	68

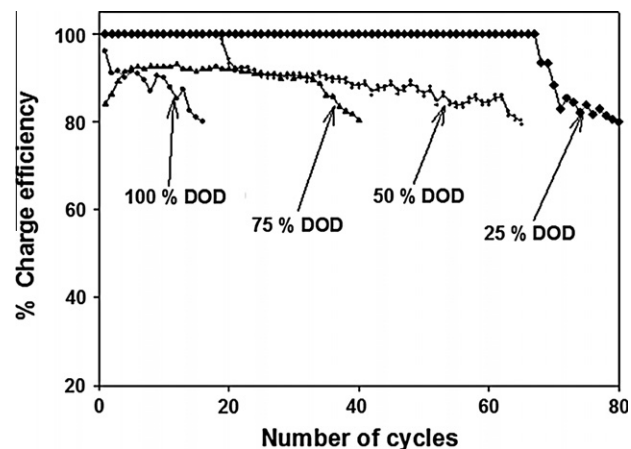


Fig. 10. Life cycle characteristics (% charge efficiency vs. number of cycles) of a soluble lead-acid flow battery at different depth of discharge (DOD) values in the range 25–100%. Electrolyte: $0.5 \text{ mol dm}^{-3} \text{ Pb}(\text{CH}_3\text{SO}_3)_2 + 0.5 \text{ mol dm}^{-3} \text{ CH}_3\text{SO}_3\text{H} + 0.005 \text{ mol dm}^{-3} \text{ C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}^+$; electrolyte linear flow velocity: 2.3 cm s^{-1} ; temperature: 298 K.

4.6. Environmental and related aspects

The electrolyte of soluble lead-acid flow battery is an aqueous solution of lead (II) methanesulfonate in methanesulfonic acid (MSA). MSA is more costly than sulphuric acid but it has a low toxicity and is less corrosive than sulphuric acid, making it a safer electrolyte to handle. MSA has been used in electroplating, stripping, electro-organic synthesis [34] and production of advanced materials [35]. It has particularly been studied for battery

applications due to its high purity and the absence of chloride and interfering metal cations [17]. It is also environmentally benign and can be regarded as a 'green' acid [36]; MSA is readily biodegradable according to OECD 301 A and forms carbonate and sulphate ions as final decomposition products; these are considered to be natural products in the sulphur cycle [37].

5. Conclusions

1. The electrochemistries of the soluble lead-acid flow battery and the static lead-acid battery are distinctly different; in the soluble lead acid battery lead is highly soluble in the electrolyte of methanesulfonic acid, while lead is a solid paste in the static lead-acid battery. The active material of soluble lead-acid battery is stored in a separate tank; the device may find applications in large-scale energy storage such as load levelling and smoothing of renewable energy delivery.
2. The soluble lead-acid flow battery shows as good a charge/discharge performance as the static lead-acid battery under similar conditions of current density and has acceptable charge efficiency at low current densities. In the laboratory prototype soluble lead-acid flow battery large overpotentials were observed. These large overpotentials at the positive electrode may be reduced by cell design and optimisation.
3. In a similar fashion to the static lead-acid battery, some self-discharge is clearly observed after leaving the soluble lead-acid battery on open-circuit for a long time. But it can recover to normal charge efficiency after one charge and discharge cycle.
4. The cycle life of the two batteries is strongly influenced by the depth of discharge. The soluble lead-acid flow test cell was found to have a relatively low cycle life. However, the addition of dissolved oxygen or hydrogen peroxide to the electrolyte can successfully resolve the problem of shorting caused by lead deposition, and the life of soluble lead-acid flow battery can be considerably extended.
5. From the environment protection point of view, the soluble lead-acid battery employs methanesulfonic acid as electrolyte, and this acid is considered to be environmental friendly and biodegradable.
6. The soluble lead-acid battery is still in its infancy, and significant work is needed to optimise its electrochemistry and engineering.

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References

- [1] Hussain ZF. Current control of three-phase PWM inverters for flywheel energy storage systems. PhD Thesis, University of Southampton; 2000.
- [2] Rydh CJ, Sandén BA. Energy analysis of batteries in photovoltaic systems. Part I: performance and energy requirements. *Energy Convers Manage* 2005;46: 1957–79.
- [3] Rydh CJ, Sandén BA. Energy analysis of batteries in photovoltaic systems. Part II: energy return factors and overall battery efficiencies. *Energy Convers Manage* 2005;46:1980–2000.
- [4] Jenkins DP, Fletcher J, Kane D. Model for evaluating impact of battery storage on microgeneration systems in dwellings. *Energy Convers Manage* 2008;49: 2413–24.
- [5] Chakrabarti MH, Roberts EPL, Bae C, Saleem M. Ruthenium based redox flow battery for solar energy storage. *Energy Convers Manage* 2011;52:2501–8.
- [6] Zhu WH, Zhu Y, Tatarchuk BJ. A simplified equivalent circuit model for simulation of Pb-acid batteries at load for energy storage application. *Energy Convers Manage* 2011;52:2794–9.
- [7] Kordesch KV. Batteries. New York: Marcel Dekker; 1974.
- [8] Walsh FC. Electrochemical technology for environmental treatment and clean energy conversion. *Pure Appl Chem* 2001;73:1819–37.
- [9] De Léon CP, Frías-Ferrer A, González-García J, Szánto DA, Walsh FC. Redox flow cells for energy conversion. *J Power Sources* 2006;160:716–32.
- [10] Yang ZG et al. Electrochemical energy storage for green grid. *Chem Rev* 2011;111:3577–613.
- [11] Price A, Bartley S, Male S, Cooley G. A novel approach to utility-scale energy storage. *Power Eng J* 1999;13:122–9.
- [12] Sum E, Skyllas-Kazacos M. A study of the V(II)/V(III) redox couple for redox flow cell applications. *J Power Sources* 1985;15:179–90.
- [13] Kear G, Shah AA, Walsh FC. Development of the all-vanadium redox flow battery for energy storage: a review of technological, financial and policy aspects. *Int J Energy Res* 2011. doi:10.1002/er.186 [published electronically].
- [14] Skyllas-Kazacos M, Limantari Y. Kinetics of the chemical dissolution of vanadium pentoxide in acidic bromide solutions. *J Appl Electrochem* 2004;34:681–5.
- [15] Lim HS, Lackner AM, Knechtli RC. Zinc-bromine secondary battery. *J Electrochem Soc* 1977;124:1154–7.
- [16] Leung PK, Ponce-de-leon C, Waslsh FC. Characterization of a zinc-cerium flow battery. *J Power Sources* 2011;196:5174–85.
- [17] Hazza A, Pletcher D, Wills RGA. A novel flow battery: a lead acid battery based on an electrolyte with soluble lead (II) – Part I. Preliminary studies. *Phys Chem Chem Phys* 2004;6:1773–8.
- [18] Pletcher D, Wills RGA. A novel flow battery: a lead acid battery based on an electrolyte with soluble lead (II) – Part II. Flow cell studies. *Phys Chem Chem Phys* 2004;6:1779–85.
- [19] Pletcher D, Wills RGA. A novel flow battery—a lead acid battery based on an electrolyte with soluble lead (II) – III. The influence of conditions on battery performance. *J Power Sources* 2005;149:96–102.
- [20] Hazza A, Pletcher D, Wills RGA. A novel flow battery—a lead acid battery based on an electrolyte with soluble lead (II) – IV. The influence of additives. *J Power Sources* 2005;149:103–11.
- [21] Pletcher D, Zhou H, Kear G, Low CTJ, Walsh FC, Wills RGA. A novel flow battery—a lead-acid battery based on an electrolyte with soluble lead(II) – V. Studies of the lead negative electrode. *J Power Sources* 2008;180:621–9.
- [22] Pletcher D, Zhou H, Kear G, Low CTJ, Walsh FC, Wills RGA. A novel flow battery—a lead-acid battery based on an electrolyte with soluble lead(II) – Part VI. Studies of the lead dioxide positive electrode. *J Power Sources* 2008;180: 630–4.
- [23] Li X, Pletcher D, Walsh FC. A novel flow battery: a lead acid battery based on an electrolyte with soluble lead(II): Part VII. Further studies of the lead dioxide positive electrode. *Electrochim Acta* 2009;54:4688–95.
- [24] Collins J, Kear G, Li X, Low CT, Pletcher D, Tangirala R, et al. A novel flow battery: a lead acid battery based on an electrolyte with soluble lead (II) Part VIII. The cycling of a 10 cm × 10 cm flow cell. *J Power Sources* 2010;195: 1731–8.
- [25] Collins J, Li X, Pletcher D, Tangirala R, Stratton-Campbell D, Walsh FC, et al. A novel flow battery: a lead acid battery based on an electrolyte with soluble lead (II). Part IX: electrode and electrolyte conditioning with hydrogen peroxide. *J Power Sources* 2010;195:2975–8.
- [26] Wills RGA, Collins J, Stratton-Campbell D, Low CTJ, Pletcher D, Walsh FC. Developments in the soluble lead-acid flow battery. *J Appl Electrochem* 2010;40(5):955–65.
- [27] Low CTJ, Pletcher D, Walsh FC. The electrodeposition of highly reflective lead dioxide coatings. *Electrochem Commun* 2009;11:1301–4.
- [28] Li X, Pletcher D, Walsh FC. Electrodeposited lead dioxide coatings. *Chem Soc Rev* 2011;40:3879–94.
- [29] Kuhn AT. The electrochemistry of lead. New York: Academic Press; 1979.
- [30] Doerffel D, Sharkh SM. A critical review of using the Peukert equation for determining the remaining capacity of lead-acid and lithium-ion batteries. *J Power Sources* 2006;155:395–400.
- [31] Ruestchi P. Review on the lead-acid battery science and technology. *J Power Sources* 1977;2:3–24.
- [32] Linden D, Reddy TB. In: Alvin J, editor. Handbook of batteries. New York: McGraw Hill; 2002.
- [33] Regenesys utility scale energy storage. Project summary DTI/Pub URN 04/1048. Inc. <<http://www.berr.gov.uk/files/file16056.pdf>> [accessed 13.06.09].
- [34] Devadoss V, Noel M, Jayaraman K, Ahmed Basha C. Electrochemical behaviour of Mn³⁺/Mn²⁺, Co³⁺/Co²⁺ and Ce⁴⁺/Ce³⁺ redox mediators in methanesulfonic acid. *J Appl Electrochem* 2003;33(3–4):319–23.
- [35] Klausjorg K, Kohhirt W. Cathodic electrodeposition coatings, their production and their use. United States Patent 6541,120; 2001.
- [36] Gernon MD, Wu M, Buszta T, Janney P. Environmental benefits of methanesulfonic acid: comparative properties and advantages. *Green Chem* 1999;1:127–40.
- [37] Baker SC, Kelly DP, Murrell JC. Microbial degradation of methane sulphonic acid: the missing link in the biogeochemical sulphur cycle. *Nature* 1991;350: 627–8.